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Reaction of Oxygen Atoms with Dimethyl Ether

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Reaction products have been examined in the gas phase reaction of dimethyl ether and oxygen atoms produced by the mercury photo-sensitized decomposition of nitrous oxide.

Based on the observed products, of which water, methanol, formaldehyde, methyl cellosolve and ethylene glycol dimethyl ether are of importance, the H abstraction of ether has been postulated as a major step of O atom attack.

According to the proposed scheme, the rate constant of the reaction $O+CH_3OCH_3 \xrightarrow{k_E} OH+CH_3OCH_2$ has been obtained in the competitive reaction with *n*-butane: $k_E=2.35\times10^9 \exp(-2600/RT)$ l, mol^{-1}, sec^{-1}.

INTRODUCTION

Whereas the reactions of O atoms with olefins have been investigated extensively in recent years, chiefly by Cvetanović and his co-workers[1,2,3], papers dealing with the reactions with saturated molecules seem quite scanty in which almost all the substrates are paraffins[2,3,4,5], and as for the oxygen compounds only few papers[6,7] are available for formaldehyde and acetaldehyde except the classical observations of Geib or Harteck[8].

As can be seen from the results of the above workers[1-e,i) 2,3,4,5], the addition of O atom to the olefinic double bond is some hundred times faster than the reaction with paraffins. However, in contrast to the fairly well established addition reaction[1-b,c,d,f,g], opinions as to the primary act of O atoms on saturates appear rather divergent; H atom abstraction by O atom, $RH+O \rightarrow HO+R$, has been often suggested[7,8], but on the other hand elementary steps such as the simultaneous replacement of two groups of the substrate, e.g., $Me_3CH+O \rightarrow Me_3CO+H+CH_3$ or Me_3CO+CH_4[4], and insertion of O between C-H, e.g., $CH_3CHO+O \rightarrow CH_3COOH$[6] have been preferred recently, but in each case the condition differs markedly. Thus, a number of observations need to be gathered before the matter becomes settled.

In this respect, we have intended to investigate the reaction of O atom with a series of oxygen compounds, and for the first have chosen dimethyl ether (abbreviated as DME hereafter) as a representative and tried to reveal the primary act of O atom based on the product analyses and also to get the rate constant of this step in comparison with that for paraffinic hydrocarbon.

As a source of O atoms the mercury photo-sensitized decomposition of nitrous oxide was utilized which has been stated to produce the oxygen atom

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of ground electronic state from the consideration on spin conservation rule, viz.,

$$Hg(^1S_0)+h\nu(2537Å) \longrightarrow Hg^*(^3P_1),$$
$$Hg^*(^3P_1)+N_2O \longrightarrow Hg(^1S_0)+N_2+O(^3P_1)^{1-c)\ 16,17)}.$$

Additional studies have been made on the mercury photo-sensitized decomposition of DME and also on the photo-induced reaction of H_2O_2 with DME, and together with these observations it has been shown that the H atom abstraction is at least one of the most probable reaction of O atom attack. Further, from the result of the competitive reaction with *n*-butane, the rate constant of O atom attack has been obtained, the numerical value of which being nearly the same as that of *n*-butane.

EXPERIMENTAL

Apparatus

All experiments were conducted under the static conditions. In a glass reactor (88 mmϕ×612 mm, 3290 cc) a low pressure mercury lamp (Toshiba Electric Co. germicidal lamp GL 15, dc operated, 15 watt, 25 mmϕ×436 mm) was placed coaxially, which was enclosed in a Vycor glass cylinder sheath in order to cut off the light shorter than 2200Å, electrical leads being connected through hermetic seals. A thermocouple was also inserted into the reactor through hermetic seal and the whole vessel was mounted in a box internally heated with nichrome wire.

The positional temperature difference in this box was maintained less than ±2°C by means of forced air circulation by a fan. Auxiliary parts such as vacuum system, manometers, Toepler pump and gas burrettes were as usual.

General Procedure

A few drops of mercury was introduced in the reactor, and after evacuation to about 10^{-3} mmHg, the reactants were fed successively from the reservoirs while the pressure were measured by mercury manometers.

At the end of the exposure of a definite duration under fixed temperature the gaseous products were drawn out by Toepler pump through a trap cooled with dry ice-methanol mixture. The liquid products condensing in the vessel at room temperature were pipetted out with or without diluent, then these products were analyzed mainly by gas chromatography as shown below:

Analysis for	Column		Temp. °C
H_2	Al_2O_3	2 m	35
CO, CH_4, C_2H_6	Al_2O_3	2 m	70
O_2	Molecular sieve 5A	2 m	35
n-C_4H_{10}	Dibenzyl ether	3.6 m	29
$CH_3OCH_2CH_2OCH_3$, 1, 4 dioxane and $CH_3OCH_2CH_2OCH_2CH_2OCH_3$	Silicon oil 550	3 m	114
$CH_2(OCH_3)CH(OCH_3)CH_2(OCH_3)$	Silicon oil 550	3 m	121
HCHO	Ethofate 60/25	2 m	111

$CH_3OC_2H_5$, $CH_3OCH_2OCH_3$ and CH_3OH	D.O.P. & Polyethyleneglycol	2 m	47
H_2O and $CH_3OCH_2CH_2OH$	D.O.P. & Polyethyleneglycol	2 m	99
$CH_3OCH_2CH_2OH$	Silicon oil 550	3 m	82
	Dibenzyl ether	2 m	119
CH_3OCH_3	Dibenzyl ether	2 m	40

Qualitative detection :

HCHO	Coloration by fuchsin solution
CH_3OH	Coloration with ceric nitrate[9]
HCOOH	HgCl precipitation from $HgCl_2$ solution[10]

Materials

Nitrous oxide was prepared by heating dry ammonium nitrate[11], then condensed and degassed under vacuum in a liquid nitrogen trap after KOH washing and $CaCl_2$ drying. It was stored in gaseous state. Purity was 98.5% as determined by gas chromatography (active carbon, 2 m 92°C), the remainder was solely nitrogen.

DME was prepared from methanol by H_2SO_4 dehydration, and purified by bulb-to-bulb distillation under vacuum; purity was 99.5% as determined by gas chromatography.

79% H_2O_2 was obtained by evaporation of 30% H_2O_2 at 17 mmHg, beginning from 39° up to 47°C.

n-Butane was obtained from Takachiho Chemical Industrial Co.; garanteed purity is 99.8%.

Authentic samples for gas chromatographic identification of products :

(i) Glycerol trimethyl ether (GTE) $CH_2(OCH_3)CH(OCH_3)CH_2(OCH_3)$ was synthesized through repeated methylation of glycerin with metallic sodium and dimethyl sulfate[12].
density $d_4=0.955$ (16.5°C, obs.); 0.946 and 0.940 (15°C, litr.[12,13]).
refractive index $n_D=1.4077$ (16°C, obs.); 1.4055 and 1.4069 (15°C, litr.[12,13]).

(ii) Methyl ethyl ether was prepared by the reaction of ethyl iodide and soduim methylate[14], and purifid by bulb-to-bulb distillation.

(iii) Ethylene glycol dimethyl ether (EGDE) $CH_2OCH_2CH_2OCH_3$,

(iv) Bis-(β-methoxyethyl) ether (BMEE) $CH_3OCH_2CH_2OCH_2CH_2OCH_3$,

both samples, of reagent grade, were obtained from Tokyo Kasei Kogyo Co.

RESULTS AND DISCUSSION

Observation on the Mercury Photo-sensitized Decomposition of DME

In this study the presence of Hg in the reactor as a means of producing O atoms causes unavoidably the Hg-sensitized decomposition of the substrate, so we have to know about the products of this induced decomposition in order to discriminate the products resulting from the proper reactions of O atom. This sensitized reaction has been studied by Marcus et al.[15]; they found the presence of H_2 and $(CH_3OCH_2)_2$ and none of CO, CH_4 and RCHO at 25°C and concluded the following steps as domoninat course :

$$CH_3OCH_3+Hg(^3P_1) \longrightarrow CH_3OCH_2+H+Hg(^1S_0), \quad (1)$$

$$H+CH_3OCH_3 \longrightarrow CH_3OCH_2+H_2, \quad (2)$$

$$2CH_3OCH_2 \longrightarrow (CH_3OCH_2)_2. \quad (3)$$

In order to ascertain these facts, 200 mmHg DME was irradiated in the presence of drops of Hg at 28°C for 60 min. DME is transparent to the light longer than 2100 Å, so no photolysis takes place with the present light (≥2537 Å).

Following compounds have been identified in the products: H_2, EGDM, BMEE and GTE (as for abbreviations, see "material" of the preceding section), but no indication was obtained about the presence of CO, CH_4, C_2H_6, C_2H_4, HCHO, and 1, 4 dioxane.

The observed products agree with the scheme given above and the absence of CH_4, C_2H_6 and HCHO rules out the posibility of the decomposition of CH_3OCH_2 into CH_3+HCHO at this temperature, in accord with the results of Marcus et al.[15], further the absence of 1, 4 dioxane may suggest the non-occurrence of an H-atom loss of CH_3OCH_2 followed by recombination, viz.,

$$CH_3OCH_2+(R,\ H,\ \text{or}\ Hg^*,) \longrightarrow \cdot CH_2OCH_2\cdot \xrightarrow{\times 2} O\begin{matrix}CH_2CH_2\\ CH_2CH_2\end{matrix}O.$$

In addition, the presence of newly found GTE and BMEE would suggest the presence of the further reaction of EGDE leading to trimers of DME via $CH_3OCH_2CH_2OCH_3+(R,\ H,\ \text{or}\ Hg^*) \longrightarrow CH_3OCH_2CHOCH_3$ or $CH_3OCH_2CH_2OCH_2$, CH_2OCH_2-$CHOCH_3+CH_3OCH_2 \longrightarrow CH_3OCH_2CH(OCH_3)CH_2OCH_3$ (GTE), $CH_3OCH_2CH_2OCH_2+CH_3OCH_2 \longrightarrow CH_3OCH_2CH_2OCH_2CH_2OCH_3$ (BMEE).

Reaction of Oxygen Atom with Dimethyl Ether

In order to search for the reaction products, mixtures of 100 mmHg DME and 300 mmHg N_2O were irradiated for 30~60 min. at 20~35°C in the presence of Hg drops. In the preliminary runs it was observed that, when DME was present at least 1/80 of N_2O at the beginning of the irradiation, no oxygen molecule could be found in the product even after the initially charged DME had vanished by prolonged exposure. This is in agreement with the result of Cvetanović[16], and the reaction of O atom with the substrate seems much faster than the oxygen forming reactions of O atom in pure N_2O, of which little has been known[16].

Following products were identified: H_2, CH_3OH, H_2O, HCHO, HCOOH, $CH_3OCH_2CH_2OH$ (methyl cellosolve), EGDE, BMEE, GTE, but any of CO, CH_4, C_2H_6, C_2H_4, O_2, $CH_3OCH_2OCH_3$ (methylal), $CH_3OC_2H_5$, and 1, 4 dioxane could not be found.

Based on the observed products the following consideration may be put forward on the course of the reaction.

(a) The formation of H_2O seems to be nicely explained by assuming the intermediation of OH radical which has resulted from the H-abstraction reaction of O atom, viz.,

$$O+CH_3OCH_3 \longrightarrow OH+CH_2OCH_3, \quad (4)$$

$$OH+RH \longrightarrow H_2O+R\ (RH\ \text{is any H-containing molecule or radical.}) \quad (5)$$

We might suppose that the water has originated from H atom produced by

Hg photo-sensitized decomposition of DME or by other processes such as described below, through the reaction with the co-existing N_2O, $H+N_2O \rightarrow OH+N_2+60.3$ kcal (6), or through the combination with O atom, $O+H+M \rightarrow OH+M$. However, these must not be the case here as discussed next.

The rate constant of (6) can be estimated from the result of Fenimore and Jones[18] (N_2O+H_2 Flame, ca. 1200°C) and of Schiavello and Volpi[19] (H_2 microwave discharge$+N_2O$, 150°C). A very long range extrapolation of the formers' rate constant, $k=4\times10^{11}\exp(-16300\pm2000)/RT$ l, mol^{-1}, sec^{-1}, to 28°C gives $k=17$ l, mol^{-1}, sec^{-1} as the upper limit, and from the latters' rough estimation, $k\simeq10^4$ at 150°C, $k\leq6.6$ l, mol^{-1}, sec^{-1} at 28°C is derived using the Fenimore's activation heat. On the other hand, Trost et al.[20] have given the collision yield of the reaction (2) as $(5\sim10)\times10^{-7}$ at 25°C, which leads to $k=10^5$ l, mol^{-1}, sec^{-1} as the lower value. Therefore, under the present experimental condition where the amount of DME is about 1/3 of co-existing N_2O, reaction (2) is by far predominant in competition with (6) and the posibility of H_2O formation through $H+N_2O$ becomes much reduced.

Combination rate constant of O and H by three body collision must be of the order of 10^{10} l^2, mol^{-2}, sec^{-2} by analogy with the reactions $O+O+M$[21] and $H+H+M$[22]; this leads to $\left(\frac{-d(O)}{dt}\right)_{(OH)}\simeq2\times10^8(O)(H)$ mol, l^{-1}, sec^{-1} under the present pressure of the third body. On the other hand, as shown later, the rate of O atom disappearance by the reaction with DME must be of the order of $\left(\frac{-d(O)}{dt}\right)_{(DME)}=3\times10^7(O)(DME)$ mol, l^{-1}, sec^{-1}.

Since $(H)\ll(DME)$, OH formation by recombination must play only negligible role, if any, in the water formation.

Further, we may write down some schemes producing H_2O in one act which necessarily accompany biradical formation, e.g.,

$$O+CH_3OCH_3 \longrightarrow O:\begin{matrix}\cdot H\cdot\\ :CHOCH_3\\ \cdot H\cdot\end{matrix} \longrightarrow H_2O+{:}CHOCH_3, \qquad (7)$$

$$\text{or} \longrightarrow O:\begin{matrix}\cdot H\cdots CH_2\\ \diagdown\!\!\diagup O\\ \cdot H\cdots CH_2\end{matrix} \longrightarrow H_2O+\cdot CH_2OCH_2. \qquad (8)$$

Absence of 1, 4 dioxane in the product argues against the scheme (8), and, though with some reservation, we may say that the analogous biradical formation process (7) also must be improbable. Stepwise formation of H_2O without passing through OH seems quite implausible.

(b) The presence of MeOH and HCHO might be explained by assuming to have been resulted from the fission of O-C bond by O atom, viz.,

$CH_3OCH_3+O \longrightarrow CH_3O+CH_3O$, or CH_3O+CH_2O+H,
$CH_3O+RH \longrightarrow CH_3OH+R$,
$CH_3O \longrightarrow HCHO+H$.
($CH_2OCH_3 \longrightarrow CH_3+HCHO$ has been ruled out in the preceding section.)

But, if this be the case we would well expect the formation of CH_4, C_2H_6, CO, $CH_3OCH_2OCH_3$ and $CH_3OC_2H_5$ by the succeding reactions of CH_3O and CH_3,

and HCHO photo-reaction :

$$HCHO \xrightarrow{h\nu} H+CHO \longrightarrow CO+H,$$
$$CH_3O+CH_3OCH_2 \longrightarrow CH_3OCH_2OCH_3,$$
$$CH_3+CH_3OCH_2 \longrightarrow CH_3OC_2H_5,$$

whereas, none of these expectable products is found.

On the other hand, these facts can be explained consistently by assuming the formation of hemiacatal, CH_3OCH_2OH, in the gas phase, which, in the reactor by the produced water and/or during the analytical procedure by the added water, is hydrolyzed into MeOH and HCHO and caught as such. Of course, CH_3OCH_2OH has not been isolated heretofore, but it is well conceivable to be produced once as a labile species *in the gas phase.*

The presence of methyl cellosolve also can be understood analogously as resulted from EGDE by this assumption, viz.,

$$O+CH_3OCH_3 \cdots\cdots\rightarrow CH_3OCH_2OH \xrightarrow{+H_2O} CH_3OH+HCHO,$$
$$O+CH_3OCH_2CH_2OCH_3 \cdots\cdots\rightarrow CH_3OCH_2CH_2OCH_2OH \xrightarrow{+H_2O} CH_3OCH_2CH_2OH+HCHO.$$

We are here to assume the formation of hemiacetal in this system; then, there are at least three possibilities which result in hemiacetal formation·

Scheme I $CH_3OCH_3+O \longrightarrow CH_3OCH_2+OH,$
$CH_3OCH_2+OH \longrightarrow CH_3OCH_2OH.$

Scheme II $CH_3OCH_3+O \longrightarrow CH_3O\overset{H_2}{\underset{\vdots O \vdots}{C}}\cdots H \longrightarrow CH_3OCH_2OH$ (insertion of O atom between C and H).

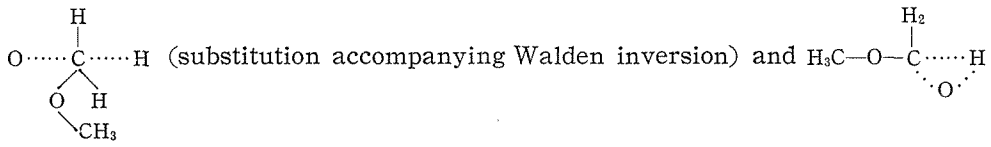
Scheme III $CH_3OCH_3+O \longrightarrow CH_3OCH_2O+H,$
$CH_3OCH_2O+RH \longrightarrow CH_3OCH_2OH+R.$

Of these, the first step of the scheme I has already been discussed, and the second step, i.e., the combination of OH and CH_3OCH_2 has been proved clearly to occur in the photo-induced reaction of H_2O_2 with DME as described in the next section. Thus it is evident the Scheme I is one of the plausible process.

Scheme II is the insertion reaction as is well known in the reaction of CH_2 with saturated molecules. It has been suggested, however, that the CH_2 will insert into C-H bond if its electronic state is singlet, and if it is in triplet state it will abstract H atom from the substrate[23]. Since the electronic state of O atom is considered to be triplet in the present case it would be natural to expect the O atom to abstract H rather than to insert. Further, in this scheme no H_2O formation can be explained.

Concerning the scheme III Wright[1] has proposed in the reaction of O atom with *i*-butane a mechanism in which O atom replaces H atom according to $O+C-\overset{C}{\underset{C}{C}}-H \longrightarrow C-\overset{C}{\underset{C}{C}}-O+H$; this is the case for the scheme III. One criterion on this scheme is to find out the H_2 thus produced; unfortunately, H_2 is otherwise produced by the Hg photo-sensitized decomposition of DME and no discrimination is possible in the present stage of investigation. From the con-

sideration on spin, this reaction is possible provided the produced radical and H atom are both in doublet which seems quite natural, and we may think of two types of activated complex, viz.,



(substitution accompanying Walden inversion) and

as in scheme II. Since the formation of CH_3OCH_2OH is highly exothermic, the latter complex may be capable of being further decomposed before collisional stabilization. But, as is shown above the H atom thus produced does not contribute to the H_2O formations, so, here too the H_2O formation cannot be explained by this scheme.

According to the preceding arguments, it seems most probable to the authors the preferential occurrence, if not exclusive, of H abstraction of DME as the primary act of O atom, and in this way we are to propose the following scheme as one of the most plausible process:

$O(^3P_1)+CH_3OCH_3 \longrightarrow CH_3OCH_2+OH$,
$OH+CH_3OCH_3 \longrightarrow CH_3OCH_2+H_2O$,
$OH+CH_3OCH_2 \longrightarrow CH_3OCH_2OH$,
$(CH_3OCH_2OH+H_2O \longrightarrow CH_3OH+HCHO)$,
$2CH_3OCH_2 \longrightarrow CH_3OCH_2CH_2OCH_3$,
$CH_3OCH_2CH_2OCH_3+O$ (or OH) $\longrightarrow CH_3OCH_2CH_2OCH_2+OH$ (or H_2O),
$CH_3OCH_2CH_2OCH_2+OH \longrightarrow CH_3OCH_2CH_2OCH_2OH$,
$(CH_3OCH_2CH_2OCH_2OH+H_2O \longrightarrow CH_3OCH_2CH_2OH+HCHO)$,
$CH_3OCH_2CH_2OCH_3+O$ (or OH) $\longrightarrow CH_3OCH_2CHOCH_3+OH$ (or H_2O),
$CH_3OCH_2CHOCH_3+OH \longrightarrow CH_3OCH_2CH(OCH_3)OH$'
$(CH_3OCH_2CH(OCH_3)OH+H_2O \longrightarrow CH_3OH+CH_3OCH_2CHO)$.

The last three are added by analogy because of the presence of GTE, but no proof has been obtained for CH_3OCH_2CHO.

Photo-induced Reaction of H_2O_2 and DME for the Proof of Hemiacetal Formations

In the evacuated reactor kept at about 70°C, about 30 mmHg H_2O_2 vapor was introduced by heating 80% H_2O_2 resevoir (some H_2O vapor accompanied into the reactor), and then 200 mmHg DME was added. The mixture was irradiated by filtered Hg light ($\geq$2537 Å) as before but without Hg drops at 70°C for 60 min.

Observed products were HCHO, CH_3OH, EGDE, and $CH_3OCH_2CH_2OH$. It is known that H_2O_2 gives 2OH when photolyzed by 2537 Å light[24] (co-existing H_2O vapor does not absorb this light), and the OH will react with DME to procuce CH_3OCH_2, so if the hemiacetal formation is actually taking place by $OH+CH_3OCH_2$ as assumed before we can expect to observe CH_3OH and HCHO on analysis and also methyl cellosolve as a consequence of the presence of EGDE. The observed evidences support this presumption strongly.

Rate Constant for the Reaction $O+CH_3OCH_3$

From the forgoing discussion we assume here that the reaction of O atom with DME is solely the abstraction of H atom,

$$O+CH_3OCH_3 \xrightarrow{k_E} HO+CH_3OCH_2.$$

On the other hand, resultant OH also attacks DME,

Table 1. Reactions at 28°C

Initial Pressure	Total	mmHg	351.7	336.5	319.0	225.8
	DME	mmHg	50.0	31.0	9.5	7.1
		%	14.2	9.21	2.98	3.14
	n-C_4H_{10}	mmHg	31.7	20.1	7.3	5.8
		%	9.01	5.97	2.29	2.57
	N_2O	mmHg	270.0	285.4	302.2	212.9
		%	76.8	84.8	94.7	94.3
Irradiation		min.	60	77	30	30
Final Pressure	Total	mmHg	343.5	330.0	318.0	223.5
	DME	mmHg	26.5	7.6	5.6	2.6
		%	7.72	2.30	1.77	1.15
	n-C_4H_{10}	mmHg	17.7	5.7	4.4	2.3
		%	5.17	1.72	1.39	2.56
α			1.09	1.11	1.05	1.10
$k_E(=\alpha k_B)\times10^{-7}$			3.03	3.09	2.92	3.16

$k_{E\,mean}=3.05\times10^7$ l, mol^{-1}, sec^{-1}.

$\alpha\equiv\ln\frac{(DME)_0}{(DME)_t}\Big/\ln\frac{(n\text{-}C_4H_{10})_0}{(n\text{-}C_4H_{10})_t}$, $k_B(28°)=2.78\times10^7$ l, mol^{-1}, sec^{-1} [3].

Table 2. Reactions at various temperatures.

React. Temp. °C			50	63	95.5	132	152
Initial Pressure	Total	mmHg	251.0	243.1	279.0	279.7	270.0
	DME	mmHg	16.2	7.4	17.3	9.7	20.2
		%	6.45	3.04	6.20	3.47	7.49
	n-C_4H_{10}	mmHg	15.2	7.5	17.0	14.7	15.8
		%	6.05	3.08	6.09	5.25	5.85
	N_2O	mmHg	219.6	228.2	254.7	253.3	234.0
		%	87.5	93.9	87.7	91.3	86.7
Irradiation		min.	60	30	60	30	60
Final Pressure	Total	mmHg	253.0	244.2	276.5	281.0	273.5
	DME	mmHg	9.7	3.9	12.5	8.0	16.0
		%	3.84	1.61	4.51	2.84	5.84
	n-C_4H_{10}	mmHg	8.6	3.8	10.9	11.4	9.9
		%	3.40	1.57	3.94	4.05	3.61
α			0.895	0.944	0.740	0.550	0.515
$k_B\times10^{-7}$ (literature)[3]			4.37	5.63	9.77	16.64	20.80
$k_E\times10^{-7}$ (found)			3.91	5.31	7.23	9.15	10.70

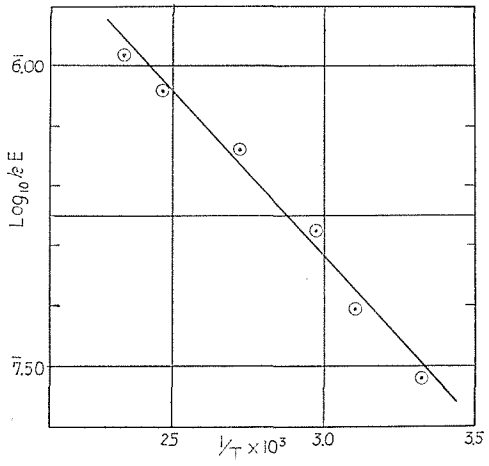


Fig. 1. Arrhenius plot of k_E.

$$OH + CH_3OCH_3 \xrightarrow{k_{E'}} H_2O + CH_3OCH_2,$$

thus,
$$\frac{-d(DME)}{dt} = \{k_E(O) + k_{E'}(OH)\}(DME),$$

or
$$\ln\frac{(DME)_0}{(DME)_t} = k_E\int_0^t (O)\,dt + k_{E'}\int_0^t (OH)\,dt,$$

where subscript 0 or t denotes time $=0$ or t, respectively.

In place of determining (O) or (OH), the competitive method has been utilized in which the reaction was conducted under the co-existence of n-butane. Elias and Schiff[3] has determined the rate constant of the reaction between n-C_4H_{10} and O atom as $(3.01\pm0.95)\times10^{10}\exp(-4200/RT)$ l, mol^{-1}, sec^{-1} based on the measurement of the disappearing rate of butane, and although they did not tell about the reaction product of the elementary step, they considered the rate constant not to be involved by other DME-consuming reactions under their conditions.

So, we are to understand their rate constant as k_B in the next scheme according to our consideration,

$$O + C_4H_{10} \xrightarrow{k_B} OH + C_4H_9,$$
$$OH + C_4H_{10} \xrightarrow{k_{B'}} H_2O + C_4H_9.$$

Then, as above,

$$\ln\frac{(C_4H_{10})_0}{(C_4H_{10})_t} = k_B\int_0^t (O)\,dt + k_{B'}\int_0^t (OH)\,dt,$$

Now we can determine experimentally the ratio α defined by

$$\alpha = \ln\frac{(DME)_0}{(DME)_t} \Big/ \ln\frac{(C_4H_{10})_0}{(C_4H_{10})_t} = \frac{\left\{\int_0^t (O)\,dt + \frac{k_{E'}}{k_E}\int_0^t (OH)\,dt\right\}k_E}{\left\{\int_0^t (O)\,dt + \frac{k_{B'}}{k_B}\int_0^t (OH)\,dt\right\}k_B}$$

Here, in order to utilize this equation we have to put a tentative assumption, $k_{E'}/k_E = k_{B'}/k_B$; difference between free O atom and OH radical in the

interaction between the same reaction centers, i.e., the attacking O atom and the C-H bond to be broken, would be considered to be nearly the same for each substrate. If the above relation holds, though not exactly but to the extent enough to cancel the parentheses of this equation, we get $\alpha = k_E/k_B$, and can obtain the absolute value of k_E in reference to k_B.

The experimental conditions were: initial pressures, $(DME)_0$ 7~50 mmHg, $(n\text{-}C_4H_{10})_0$ 5~30 mmHg, $(N_2O)_0$ 210~300 mmHg, and irradiation time 30 or 60 min. Decreas of the absolute amount of DME and butane was determined by pressure measurements with manometers along with gas chromatographical composition analyses of the product gases.

The results are shown in Table 1; from numerical value of α we can say that k_E and k_B are nearly the same under the temperature range examined, and the mean value of k_E is 3.05×10^7 l, mol^{-1}, sec^{-1} at 28°C.

The rate constants under various temperatures are given in Table 2 and also the Arrhenius plot in Fig. 1; from the slope we get the activation heat as 2.6 kcal, and finally $k_E = 2.35\times10^9 \exp(-2600/RT)$ l, mol^{-1}, sec^{-1}.

It should, however, be remembered that in the process to obtain this value two assumptions have been included, i.e., DME and C_4H_{10} disappear solely by the H abstraction reactions with O and OH, and k_E/k_E' is nearly equal to k_B/k_B', the latter may be hardly accepted without reservation.

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